



11) Publication number:

0 563 460 A1

(2) EUROPEAN PATENT APPLICATION

(21) Application number: 92200961.8 (51) Int. Cl.⁵: C11D 3/39

② Date of filing: 03.04.92

Date of publication of application:06.10.93 Bulletin 93/40

Designated Contracting States:
AT BE CH DE DK ES FR GB GR IT LI LU NL PT
SE

7) Applicant: THE PROCTER & GAMBLE COMPANY
One Procter & Gamble Plaza
Cincinnati Ohio 45202(US)

② Inventor: Hardy, Frederick Edward

8 Woodend, Darras Hall

Ponteland, Newcastle upon Tyne NE20

9ES(GB)

Inventor: Scialla, Stefano (NMN)

Viale dei Caduti nella Guerra di Liberazione

131

I-00128 Rome(IT)

Inventor: Scoccianti, Raffaele (NMN)

Viale Trastevere, 26 I-00153 Rome(IT)

Inventor: Manfredi, Barbara (NMN)

Via Saleno, 14 I-00162 Rome(IT)

Representative: Canonici, Jean-Jacques et al Procter & Gamble European Technical Center N.V. Temselaan 100

B-1853 Strombeek-Bever (BE)

Acidic activated bleaching composition.

Aqueous bleaching compositions are disclosed which comprise hydrogen peroxide as well as an organic peracid precursor selected from a specific class of glycol and glycerin esters. The compositions have a pH in the range of from about 3.5 to about 6. The disclosed compositions are both physically and chemically stable.

Technical field

The present invention relates to bleaching compositions, mainly for use in laundry applications. The compositions according to the present invention, which comprise hydrogen peroxide as well as peracid precursors, are stable upon storage.

Background

5

15

30

35

40

45

50

Bleaching compositions using hydrogen peroxide have been extensively described in the art. Such hydrogen peroxide bleaches have an advantage over chlorine bleaches in that they are environmentally more compatible. Another advantage is that they are "milder" bleaches. This latter advantage is especially significant in laundry applications as hydrogen peroxide bleaches are safer to fabrics.

A major drawback of hydrogen peroxide bleaches is that they are less active than chlorine bleaches at low temperatures which are often encountered in modern laundering applications. Thus, hydrogen peroxide bleach activators have been developed and have been extensively described in the art. These activators are mainly transition metals or peracid precursors. Peracid precursors react with hydrogen peroxide to yield peracids. Peracids are the "activated" bleaching compounds which are efficient at low temperatures.

A problem which occurs in the formulation of such "activated" hydrogen peroxide bleaching compositions is the difficulty to obtain a composition which is both chemically and physically stable. Indeed, such compositions of the prior art are either turbid suspensions of insoluble activators with good chemical stability, or clear compositions with poor chemical stability which causes significant and undesired oxygen release.

It has now been found that this problem could be addressed by formulating a bleaching composition comprising hydrogen peroxide, an organic peracid precursor selected from a specific class, e.g. glycol and glycerin esters, and by formulating said composition in a narrow, acidic pH range. The mildly acidic pH range allows for adequate chemical stability of both the hydrogen peroxide and the organic peracid precursor. The activation of hydrogen peroxide trough the formation of a peracid is enhanced by the pH raise which occurs upon dilution in the wash water, especially when a detergent composition bringing further alkalinity is also present in the wash water.

Glycol esters have been often described as solvents in detergent and bleaching compositions. Such compositions are described for instance in US 3 956 159. These compositions have a pH of 6.5 and above.

J 62252500 (abstract) discloses bleaching compositions which comprise a bleach activator, including triacetin. These compositions are formulated at neutral or weakly basic pH.

Bleaching compositions for various applications, comprising triacetin are also disclosed in J62001792, J62001794 J 62001796, and J61042600 (abstracts).

Summary of the invention

The compositions according to the present invention are clear aqueous bleaching compositions comprising hydrogen peroxide as well as an organic peracid precursor, characterized in that the compositions have a pH in the range of from about 3.5 to about 6, and that the organic peracid precursor is a compound according to the formula:

 $\begin{array}{c|cccc}
CH_2 & CH_2 & CH_2 \\
 & | & | & | \\
 R_1 & R_2 & R_3
\end{array}$

wherein x is 0 or 1, R₁, R₂, R₃ are independently selected from -H, -OH,

55 -C-O-R, || O or

5

10

25

30

35

where R_4 is $C_1\text{-}C_4$ alkyl, with the proviso that at least two of R_1 , R_2 or R_3 are

or mixtures thereof.

15 Detailed description of the invention

The compositions according to the present invention are clear aqueous liquid compositions which comprise hydrogen peroxide. Preferably, the compositions according to the present invention comprise from about 0.5 % to about 20 % by weight of the total composition of hydrogen peroxide, more preferably from about 2 % to about 15 %, most preferably from about 4 % to about 9%.

The compositions according to the present invention further comprise a specific organic peracid precursor according to the formula:

wherein x is 0 or 1, R₁, R₂, R₃ are independently selected from -H, -OH,

-C-O-R₄

40 or

45

50

55

-o-c-R₄

where R_4 is C_1 - C_4 alkyl, with the proviso that at least two of R_1 , R_2 or R_3 are

-0-**C-**R₄;

or mixtures thereof. All these compounds are well known chemicals which are commercially available or can be synthesized according to the chemical literature.

Preferred such peracid precursors for use in the compositions according to the present invention are selected from ethylene glycol diesters, triacetin and diacetin, or mixtures thereof. Particularly preferred compounds are triacetin and ethylene glycol diacetate. Tributyrin also displays excellent stability in the compositions according to the present invention but is less preferred because it is less soluble in the

compositions according to the present invention.

The compositions according to the present invention typically comprise from about 1 % to about 15 % by weight of the total composition of such an organic peracid precursor, or mixtures thereof. The desired amount of organic peracid precursor can also be defined in relation to the amount of hydrogen peroxide in the composition. Accordingly, the compositions according to the present invention preferably comprise from about 0.1 to about 2 moles of organic peracid precursor per mole of hydrogen peroxide.

The compositions according to the present invention have a pH in the range of from about 3.5 to about 6, most preferably from about 3.5 to about 5, most preferably about 4. The pH of the composition can be adjusted and buffered with such chemicals as organic and inorganic acids which are stable to oxidation, citric acid, sulphuric acid, sodium hydroxide, ammonia and amines. Preferred buffer for use in the compositions according to the present invention is citric acid. It is essential that the pH of the composition remains within the above range as said range is critical to ensure adequate chemical stability of the hydrogen peroxide and of the specific organic peracid precursors used in the compositions according to the present invention.

The compositions according to the present invention may comprise surfactants. Preferred surfactants for use herein are well known anionic surfactants such as alkyl benzene sulphonates and alkyl sulfates, and/or nonionic surfactants such as ethoxylated and/or propoxylated alcohols. All surfactants for use herein must be resistant to oxidation by peracids and hydrogen peroxide, and are preferably water-soluble. The compositions according to the present invention can comprise from 0% to about 30% by weight of the total composition of surfactants, preferably from about 0.5 % to about 15 %, most preferably from about 2 % to 8 %.

The compositions according to the present invention may further comprise peroxide stabilizers such as stannates, 8-hydroxyquinoline, pyrophosphates and phosphonates. Chelating agents may also be useful in the context of the present invention; suitable chelants include EDTA, NTA and DETPA, picolinic and dipicolinic acids and amino polyphosphonates, although some of these are poorly environmentally compatible. Radical scavengers can also be used herein, such as butylated hydroxy toluene and other hindered hydroxy benzenes, or sodium benzoate. Butylated hydroxy toluene is a highly preferred ingredient as it has been observed that it stabilizes the peracid precursors according to the present invention, as well as hydrogen peroxide.

The compositions according to the present invention can also comprise such optional ingredients as whitening agents, dyes, builders, thickeners, hydrotropes, perfumes, all of which need to be compatible with the mildly acidic pH and the oxidizing environment of the compositions according to the present invention.

The compositions according to the present invention are further illustrated in the following examples.

Examples

15

30

35

The following compositions are made by mixing together the listed ingredients in the listed proportions.

40	Ingredients:		<pre>% by weight:</pre>			
		I	II	III	IV	
45	Hydrogen peroxide	6.0	6.0	6.0	6.0	
	Na alkyl sulphate	2.8	2.8	2.8	2.8	
	Triacetin	4.0	5.0	4.0	4.0	
	Citric acid	1.0	1.0	1.0	1.0	
50	Na Stannate	0.0015	0.0010	0.0015	0.0015	
	Na hydroxide	pH 4	pH 4	pH 3.5	pH 5	pH 4
	Water & minors			up to 1	00 %	

55

EP 0 563 460 A1

	Ingredients: % by weight:			ght:	
5		v	VI	VII	VIII
	Hydrogen peroxide	6.0	8.0	3.5	5.0
10	Na alkyl sulphate	2.8	2.0	4.0	3.5
	Triacetin	_	3.0	5.0	-
	Ethylene glycol				
15	diacetate	4.0	-	-	5.0
15	Citric acid	1.0	1.0	1.0	1.0
	Na stannate	0.0015	0.0015	0.0010	0.0015
	Na hydroxide	pH 4	pH 4	pH 4	pH 4
20	Water & minors			up to 10	00 %

25 Claims

30

35

45

1. An aqueous bleaching composition comprising hydrogen peroxide and an organic peracid precursor, characterized in that the compositions have a pH in the range of from about 3.5 to about 6, and that the organic peracid precursor is a compound according to the formula:

 $\begin{array}{c|c}
CH_2 & CH_2 \\
 & | \\
 R_1 & R_2 & R_3
\end{array}$

wherein x is 0 or 1, R_1 , R_2 , R_3 are independently selected from -H, -OH,

or

where R4 is C1-C4 alkyl, with the proviso that at least two of R1, R2 or R3 are

EP 0 563 460 A1

or mixtures thereof.

- 2. A composition according to claim 1 which has a pH in the range of from about 3.5 to about 5.
- 5 3. A composition according to claim 2 which has a pH of about 4.
 - **4.** A composition according to any of the preceding claims wherein the organic peracid precursor is selected from ethylene glycol diesters, triacetin, diacetin, or mixtures thereof.
- 10 **5.** A composition according to claim 4 wherein the organic peracid precursor is selected from triacetin and ethylene glycol diacetate.
 - **6.** A composition according to any of the preceding claims which comprises from about 0.5 % to about 20 % by weight of the total composition of hydrogen peroxide.

7. A composition according to any of the preceding claims which comprises from about 1 % to about 15 % by weight of the total composition of said organic peracid precursor.

- **8.** A composition according to claim 6 which comprises from about 0.1 to about 2 moles of said organic peracid precursor per mole of hydrogen peroxide.
 - A composition according to any of the preceding claims which comprises from about 0.5 % to about 15 % by weight of the total composition of a surfactant.
- 25 10. A composition according to any of the preceding claims which comprises citric acid.
 - 11. A composition according to any of the preceding claims which comprises butylated hydroxy toluene.

55

15

30

35

40

45

50



EUROPEAN SEARCH REPORT

ΕP 92 20 0961

ategory	Citation of document with is of relevant pa	ndication, where appropriate,	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
(* page 11, line 37	EROX CHEMICALS LTD.) - page 13, line 11 * - page 23, line 36 * - line 22 *	1-6,9,10	C11D3/39
),A	DATABASE WPIL Section Ch, Derwent Publication Class D25, AN 87-04 & JP-A-62 001 794 (* abstract *	5571 [07]	1,4,5,9	
A	DATABASE WPIL Section Ch, Derwent Publication Class D25, AN 87-04 & JP-A-62 004 794 (* abstract *	6869 [07]	1,4,5,9	
				TECHNICAL FIELDS SEARCHED (Int. Cl.5)
				C11D
	The present search report has b	een drawn up for all claims Date of completion of the search		Exeminer
	THE HAGUE	26 NOVEMBER 1992		SERBETSOGLOU A.
X : par Y : par doc	CATEGORY OF CITED DOCUME rticularly relevant if taken alone rticularly relevant if combined with an nument of the same category thoological background	NTS T: theory or prin E: earlier patent after the filin other D: document cite L: document cite	ciple underlying the document, but publ g date d in the application d for other reasons	invention ished on, or

EPO FORM 1503 03.82 (P0401)

A : technological backgroun
O : non-written disclosure
P : intermediate document

&: member of the same patent family, corresponding document